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Dataset Info: Dataset ID: TTN224  
Submission Dates: Initial Submission: 20110401  
Revised Submission:  
Cruise Info:

- \* Experiment:
  - 1. Experiment Name: TN224

Cruise:

- \* Cruise ID: 325020080826
- \* Section: TN224
- \* Geographical Coverage:
  - 1. Geographical Region: Pacific Ocean

Bounds:

North	West	South	East
50.1	-157.9	18.0	-122.3

Temporal Coverage: Start Date: 20080826 End Date: 20080917  
Vessel: Vessel Name: R/V Thomas Thompson  
Vessel ID: 3250  
Country: USA  
Vessel Owner: School of Oceanography, University of Washington

Variable Name	Description of Variable
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Temperature	deg. C
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Salinity	
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Oxygen	umol/kg
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Nitrate	umol/kg
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Nitrite	umol/kg
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Silicate	umol/kg
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Phosphate	umol/kg
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CFC11, CFC12	pmol/kg
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DIC	umol/kg
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TALK	umol/kg
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#### Method Descriptions:

DIC: The DIC analytical equipment was set up in a seagoing container modified for use as a shipboard laboratory. The analysis was done by coulometry with two analytical systems (PMEL-1 and PMEL-2) used simultaneously on the cruise. Each system consisted of a coulometer (UIC, Inc.) coupled with a SOMMA (Single Operator Multiparameter Metabolic Analyzer) inlet system developed by Ken Johnson (Johnson et al., 1985, 1987, 1993; Johnson, 1992) of Brookhaven National Laboratory (BNL). In the coulometric analysis of DIC, all carbonate species are converted to CO<sub>2</sub> (gas) by addition of excess hydrogen to the seawater sample. The evolved CO<sub>2</sub> gas is carried into the titration cell of the coulometer, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. These are subsequently titrated with coulometrically generated OH<sup>-</sup>. CO<sub>2</sub> is thus measured by integrating the total charge required to achieve this.

The coulometers were each calibrated by injecting aliquots of pure CO<sub>2</sub> (99.995%) by means of an 8-port valve outfitted with two sample loops (Wilke et al., 1993). The instruments were calibrated at the beginning of each station with two sets of the gas loop injections.

Secondary standards were run throughout the cruise (at least one per station) on each analytical system. These standards are Certified Reference Materials (CRMs), consisting of poisoned, filtered, and UV irradiated seawater supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO). Their accuracy is determined shoreside manometrically. DIC data reported to the database have been corrected to the batch 89 CRM value.

Samples were drawn from Niskin-type bottles into cleaned, precombusted 540-mL Pyrex bottles using silicon tubing. Bottles were rinsed once and filled from the bottom, overflowing half a volume. Care was taken not to entrain any bubbles. The tube was pinched off and withdrawn and 0.2 mL of saturated HgCl<sub>2</sub> solution was added as a preservative. Samples were corrected for the addition of poison by a factor of 1.00037. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease, and were stored in a 20°C water bath for a minimum of 20 minutes to bring them to temperature prior to analysis.

Over 200 pure (99.995%) CO<sub>2</sub> gas calibrations were run on both SOMMA systems during this cruise. The precision and accuracy obtained from these calibrations can be described as follows:

1. The precision is estimated from ~80 replicate pairs. The absolute average difference from the mean of these replicates is 0.85 µmol/kg. No significant systematic differences were noted.
2. The accuracy is estimated from the analysis of 46 Certified Reference Materials (batch 89). The CRM value is 2025.7 µmol/kg. Our average value was 2024.7 µmol/kg with a standard deviation of 1.47 µmol/kg.

#### References:

- Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.), (2007): [Guide to Best Practices for Ocean CO<sub>2</sub> Measurements](#). PICES Special Publication 3, 191 pp.
- Johnson, K.M., A.E. King, and J. McN. Sieburth (1985): "Coulometric DIC analyses for marine studies: An introduction." Mar. Chem., 16, 61-82.
- Johnson, K.M., P.J. Williams, L. Brandstrom, and J. McN. Sieburth (1987): "Coulometric total carbon analysis for marine studies: Automation and calibration." Mar. Chem., 21, 117-133.
- Johnson, K.M. (1992): Operator's manual: "Single operator multiparameter metabolic analyzer (SOMMA) for total carbon dioxide (CT) with coulometric detection." Brookhaven National Laboratory, Brookhaven, N.Y., 70 pp.
- Johnson, K.M., K.D. Wills, D.B. Butler, W.K. Johnson, and C.S. Wong (1993): "Coulometric total carbon dioxide analysis for marine studies: Maximizing the performance of an automated continuous gas extraction system and coulometric detector." Mar. Chem., 44, 167-189.
- Lewis, E. and D. W. R. Wallace (1998) Program developed for CO<sub>2</sub> system calculations. Oak Ridge, Oak Ridge National Laboratory. <http://cdiac.ornl.gov/oceans/co2rprt.html>
- Wilke, R.J., D.W.R. Wallace, and K.M. Johnson (1993): "Water-based gravimetric method for the determination of gas loop volume." Anal. Chem. 65, 2403-2406.

Alkalinity:

Potentiometric titration was used to analyze over 900 samples, including duplicates and certified reference materials (CRM), for total alkalinity during the UW Student 2008 cruise. With the exception of the first non-test station (station 2), the analytical equipment performed well, as well as is generally expected for shipboard analyses. Reference materials were used to verify proper operation of the analytical equipment and comparison of deep samples from this cruise with historical data (<http://www.pmel.noaa.gov/co2/story/P16N>) reveal the same within analytical uncertainty.

Samples were drawn from Niskin-type bottles into cleaned, 270 mL borosilicate glass bottles using silicone tubing. Bottles were rinsed three times and filled from the bottom, overflowing by half of the bottle volume, and taking care not to entrain any bubbles. The sample tube was closed off and withdrawn from the sample bottle, leaving a 5.0 mL headspace. Samples were preserved by poisoning with 0.20 mL of a 50 percent saturated HgCl<sub>2</sub> solution. Sample bottles were sealed with ground glass stoppers lightly coated with Apiezon-L grease and stored at room temperature (21–25 °C) for a maximum of 12 hours prior to analysis.

Analysis of seawater for total alkalinity, AT, was performed using an open cell, potentiometric titration method published by Dickson et al. [2003] and subsequently adopted as one of standard analytical methods for ocean carbon measurements [Dickson et al., 2007]. By this method, a measured amount of acid titrant (0.1 m HCl) is added to the sample to reduce the pH to less than 3.55, CO<sub>2</sub>-free air is bubbled through the acidified sample to facilitate removal of the evolved CO<sub>2</sub> gas, followed by titration to a pH of less than 3.0. The titration curve is fit to a derivation of the defining equation for alkalinity in seawater using a non-linear least squares approach in which one of the adjustable parameters in the fit equation is A<sub>T</sub>. All titrations were performed at a constant temperature of 25.0 ± 0.2°C in a water-jacketed, 250 mL glass beaker. Samples were introduced into the beaker using a fixed volume (108.130 ± 0.012 mL) glass syringe. Prior to titration, all samples were brought to 25°C by placing them in a temperature-controlled water bath for at least one hour prior to analysis. After each titration, the beaker was emptied, rinsed three times with de-ionized water, and dried. Titration progress was monitored by measuring the electromotive force, E, of a combination glass-reference pH electrode (Radiometer, PHC 2002-8). Temperature during the titration was monitored using a 100Ω Pt RTD. A National Instruments<sup>TM</sup> high-precision data acquisition card (NI-4351) was used to record both titration E and T. Removal of CO<sub>2</sub> generated by acidification of the sample was accomplished by bubbling CO<sub>2</sub> free air through the sample at 100 mL min for 5 minutes. Air was dried by flowing through a Drierite column and CO<sub>2</sub> removed by flowing through an Ascarite II column. A Metrohm Dosimat 765 was used to deliver acid to the sample beaker in increments of 0.050 mL. The acid titrant used was 0.1 mol kg<sup>-1</sup> HCl prepared in 0.6 mol kg<sup>-1</sup> NaCl background to approximate the ionic strength of seawater (0.7 mol kg<sup>-1</sup>). A single batch of titrant was used over the course of the cruise: PMEL 071607-1. The acid concentration, determined gravimetrically during preparation, is 0.100190 mol kg<sup>-1</sup>. Instrument control and data acquisition was with custom software developed at NOAA/PMEL using the National Instruments LabView programming environment.

Analytical accuracy was assessed by periodic analysis of CRMs (Batch 84: supplied by Dr. A. Dickson of Scripps Institution of Oceanography; <http://andrew.ucsd.edu/co2qc/index.html>) throughout the cruise. References were analyzed approximately every 24 samples. Standard deviation over the course of the cruise is approximately 2.5 μmol kg<sup>-1</sup>. In addition, duplicate samples were taken at each station, totaling about 10% of samples analyzed, with an average standard deviation of 2.9 μmol kg<sup>-1</sup>.

#### References:

- A. G. Dickson, J. D. Afghan, and G. C. Anderson. Reference materials for oceanic CO<sub>2</sub> analysis: a method for the certification of total alkalinity. *Mar. Chem.*, 80(2-3):185–197, January 2003.
- A. G. Dickson, C. L. Sabine, and J. R. Christian, editors. [Guide to Best Practices for Ocean CO<sub>2</sub> Measurements](#). Number 3 in Special Publication. 2007.

#### Oxygen:

UW dissolved oxygen analyses were performed using a Dosimat 765 titrator and visual endpoints. Standards were dispensed using a Dosimat 665 titrator calibrated to deliver five (5) ml.

UW used a whole-bottle modified-Winkler titration following the technique of Carpenter [1965] with modifications by Codispoti. [1988]. Two KIO<sub>3</sub> standards were run every eight hours. A Wako 0.025N KIO<sub>3</sub> standard (#166-17521, 99.98% purity, Wako Pure Chemicals Ltd, 1600 Bellwood Road, Richmond, VA 23237, Phone +1 804 271 7677, Fax +1 804 271 7791, labchem@wakousa.com) was used as the primary standard. An Aldrich 0.025N KIO<sub>3</sub> standard (#7758-05-6, 99.7% ± 0.3% purity, Sigma-Aldrich Company, St. Louis, MO, USA, Phone: 314-771-5765, Fax: 314-771-5757, [cssorders@sial.com](mailto:cssorders@sial.com)) was used as a secondary standard. Reagent/distilled water blanks were determined every day or more often if a change in reagents required it to account for presence of oxidizing or reducing agents. 1876 oxygen measurements were made with duplicate samples at each of 938 distinct depths over 40 casts at 39 stations.

Samples were collected for dissolved oxygen analyses soon after the rosette was brought on board. Using a Tygon drawing tube, nominal 125ml volume-calibrated iodine flasks were rinsed 3 times with minimal agitation, then filled and allowed to overflow for at least 3 flask volumes. The sample drawing temperatures were measured with a thermistor thermometer embedded in the drawing tube. These temperatures were used to calculate umol/kg concentrations, and as a diagnostic check of bottle integrity. Reagents were added to fix the oxygen before stoppering. The flasks were shaken twice (18-20 inversions) to assure thorough dispersion of the precipitate, once immediately after drawing, and then again after about 20 minutes. The samples were analyzed within 1-4 hours of collection, and the data incorporated into the cruise database. Oxygen flask volumes were determined gravimetrically with degassed deionized water at UW.

Test Cast is listed as station 999 in data file.

#### CTD DATA:

T2 and Cond2 calibrated after cruise; T drift +0.0004 deg/yr since last cal (June 07); Cond2 drifted -.0001 PSU/mo since June 07)

Temperature in data file is from T2 and has no correction applied.

Salinity calibration with salinometer indicates S00 (Cond 1) is best salinity data

Salinity in data file is from Cond 1 aka S00.

Dana Greeley converted the ctd Oxygen data from ml/l to umol/kg with the following:

$$\text{Sbeox (ml/l)} \times 44.66 / (1 + (\text{density}) / 1000)$$

And the density was calculated from the ctd in-situ temp.

NUTRIENT DATA: Generally all data from Legs 2 (Stn 3-9) & 3 Stn (10-15) are poorer quality than leg 4 (Stn 16-39), Leg 2 H<sub>4</sub>SiO<sub>4</sub> data is bad.

Dana Greeley converted the nutrient data from umol/l to umol/kg with the following formula and assuming a constant lab temp aboard the Thompson of 25°C: 
$$y \text{ (umol/kg)} = x \text{ (umol/l)} / 1.0 + (\text{density}/1000)$$

## CHLOROFLUOROCARBON (CFC) AND SULFUR HEXAFLUORIDE (SF<sub>6</sub>) MEASUREMENTS

Analysts: Fred Menzia (JISAO, University of Washington and Marie Salmi (University of Washington)

This data report prepared by Dave Wisegarver and John Bullister, NOAA-PMEL

A PMEL analytical system was used for CFC-11, CFC-12, and sulfur hexafluoride (SF<sub>6</sub>) analyses on the 2008 University of Washington Student Cruise ('2008 Student Cruise'). About 913 seawater samples were analyzed for dissolved CFC-11, CFC-12 and SF<sub>6</sub> ('CFC/SF<sub>6</sub>') concentrations. Measurements of the concentrations of these compounds in air were also made along the cruise track.

Water samples on the 2008 Student Cruise were collected in bottles designed at PMEL with a modified end-cap to minimize water contact with the end-cap O-rings after closing. Stainless steel springs covered with a nylon powder coat were substituted for the internal elastic tubing provided with standard Niskin bottles. When taken, water samples collected for dissolved CFC-11, CFC-12, and SF<sub>6</sub> analysis were the first samples drawn from the bottles. Care was taken to coordinate the sampling of CFC/SF<sub>6</sub> with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. Samples easily impacted by gas exchange (dissolved oxygen, DIC and pH) were collected within several minutes of the initial opening of each bottle. To minimize contact with air, the CFC/SF<sub>6</sub> samples were drawn directly through the stopcocks of the bottles into 250 ml precision glass syringes equipped with three-way plastic stopcocks. The syringes were immersed in a holding tank of clean surface seawater held at ~10°C until ~20 minutes before being analyzed. At that time, the syringe was placed in a bath of surface seawater heated to ~30°C.

For atmospheric sampling, a ~75 m length of 3/8" OD Dekaron tubing was run from the CFC van located on the fantail to the bow of the ship. A flow of air was drawn through this line into the main laboratory using an Air Cadet pump. The air was compressed in the pump, with the downstream pressure held at ~1.5 atm. using a back pressure regulator. A tee allowed a flow of ~100 ml min<sup>-1</sup> of the compressed air to be directed to the gas sample valves of the CFC/SF<sub>6</sub> analytical systems, while the bulk flow of the air (>7 l min<sup>-1</sup>) was vented through the back-pressure regulator. Air samples were analyzed only when the relative wind direction was within 60 degrees of the bow of the ship to reduce the possibility of shipboard contamination. Analysis of bow air was performed along the cruise track. At each location, at least five air measurements were made to determine the precision of the measurements.

Concentrations of CFC/SF<sub>6</sub> in air samples, seawater, and gas standards were measured by shipboard electron capture gas chromatography (EC-GC) using techniques modified from those described by Bullister and Weiss (1988) and Bullister and Wisegarver (2008) as outlined below. For seawater analyses, water was transferred from a glass syringe to a glass-sparging chamber (volume ~200 ml). The dissolved gases in the seawater sample were extracted by passing a supply of CFC/SF<sub>6</sub> free purge gas through the sparging chamber for a period of 4 minutes at ~150 ml min<sup>-1</sup>. Water vapor was removed from the purge gas during passage through an 18 cm long, 3/8" diameter glass tube packed with the desiccant magnesium perchlorate. The sample gases were concentrated on a cold-trap consisting of a 1/16" OD stainless steel tube with a 5 cm section packed tightly with Porapak Q (60-80 mesh) and a 15 cm section packed with Carboxen 1000. A Neslab Cryocool CC-100 was used to cool the trap to ~-70°C. After 4 minutes of purging, the trap was isolated, and it was heated electrically to ~160°C. The sample gases held in the trap were then injected onto a precolumn (~60 cm of 1/8" O.D. stainless steel tubing packed with 80-100 mesh Porasil B, held at 80°C) for the initial separation of CFC-12, CFC-11 and SF<sub>6</sub> from later eluting peaks.

After the SF<sub>6</sub> and CFC-12 had passed from the pre-column and into the second precolumn (5 cm of 1/8" O.D. stainless steel tubing packed with MS5A, 90°C) and into the analytical column #1 (240 cm of 1/8" OD stainless steel tubing packed with MS5A and held at 80°C), the outflow from the first precolumn was diverted to the second analytical column (150 cm 1/8" OD stainless steel tubing packed with Carbograph 1AC, 80-100 mesh, held at 90°C). Column #1 and the first precolumn were held in a Shimadzu GC8 gas chromatograph with an electron capture detector (ECD) held at 340°C. Column #2 and the second precolumn were in another Shimadzu GC8 gas chromatograph with ECD held at 250°C.

The analytical system was calibrated frequently using a standard gas of known CFC/SF<sub>6</sub> composition. Gas sample loops of known volume were thoroughly flushed with standard gas and injected into the system. The temperature and pressure was recorded so that the amount of gas injected could be calculated. The procedures used to transfer the standard gas

to the trap, precolumn, main chromatographic column, and ECD were similar to those used for analyzing water samples. Four sizes of gas sample loops were used. Multiple injections of these loop volumes could be made to allow the system to be calibrated over a relatively wide range of concentrations. Air samples and system blanks (injections of loops of CFC/SF<sub>6</sub> free gas) were injected and analyzed in a similar manner. The typical analysis time for seawater, air, standard or blank samples was ~11 minutes.

Concentrations of CFC-11 and CFC-12 in air, seawater samples, and gas standards are reported relative to the SIO98 calibration scale (Cunnold et al., 2000). Concentrations of SF<sub>6</sub> in air, seawater samples, and gas standards are reported relative to the SIO2005 calibration scale (Bullister and Tanhua, 2010). Concentrations of CFC/SF<sub>6</sub> in air and standard gas are reported in units of mole fraction CFC/SF<sub>6</sub> in dry gas, and are typically in the parts per trillion (ppt) range. Dissolved CFC concentrations are given in units of picomoles per kilogram seawater (pmol kg<sup>-1</sup>) and SF<sub>6</sub> concentrations in fmol kg<sup>-1</sup>. CFC/SF<sub>6</sub> concentrations in air and seawater samples were determined by fitting their chromatographic peak areas to multi-point calibration curves, generated by injecting multiple sample loops of gas from working standards into the analytical instrument. Air samples were calibrated vs. cylinder PMEL33790 and water samples were calibrated vs. cylinder PMEL45186. The response of the detector to the range of moles of CFC/SF<sub>6</sub> passing through the detector drifted somewhat during the cruise. Full-range calibration curves were run at intervals of 4-5 days during the cruise. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently (at intervals of ~90 minutes) to monitor short-term changes in detector sensitivity.

The purging efficiency was estimated by re-purging a high-concentration water sample and measuring this residual signal. At a flow rate of 150 cc min<sup>-1</sup> for 4 minutes, the purging efficiencies were:

CFC-11    ~ 97.8%

CFC-12    ~99.6%

SF<sub>6</sub>        ~100%

Corrections for these purging efficiencies have been applied to the reported CFC/SF<sub>6</sub> concentration data.

There were an unusually large number of problems with the CFC/SF<sub>6</sub> analyses on the 2008 Student Cruise. These problems were not resolved completely during the cruise and had a significant negative impact on the overall quality of CFC/SF<sub>6</sub> data set. One recurring problem was the appearance of late eluting peaks of unknown origin on the chromatograms. Attempts were made to heat the chromatographic columns at various intervals (one to several hours) to try to reduce the impact of these peaks on the chromatograms. These efforts were only partially successful. Changes in the column injection and backflush times were also made at various times during the cruise to try to eliminate the late eluting chromatographic peaks, again with limited success. After about Station 13, it appears that one (or both) of the water and air sample run files were altered so that the injection times differed between the two kinds of samples. This may have led to a partial loss of CFC-12 extracted from the water samples. This was diagnosed from the substantially lower (by about 12%) near-surface saturation values for CFC-12 (vs. CFC-11) after about station 13. In order to try to correct for this loss of CFC-12 in seawater samples, all dissolved CFC-12 concentrations measured after station 13 have been increased by ~ 14.2% in the data report. The need for this correction is unfortunate and adds significant uncertainty to the CFC-12 values for these samples. As a consequence, the WOCE quality flags for CFC-12 in seawater samples after Station 13 which were initially set as '2' or '6' (good) have been changed to '3' (questionable).

On this expedition, based on the analysis of about 130 pairs of duplicate samples, we estimate precisions (1 standard deviation) of about 1% or 0.005 pmol kg<sup>-1</sup> (whichever is greater) for both dissolved CFC-11 and CFC-12 measurements. The estimated precision for SF<sub>6</sub> was ~3% or 0.01 fmol kg<sup>-1</sup> (whichever is greater). Overall accuracy of the measurements (a function of the absolute accuracy of the calibration gases, volumetric calibrations of the sample gas loops and purge chamber, errors in fits to the calibration curves and other factors) is difficult to estimate for this data set but may be about 2% or 0.005 pmol kg<sup>-1</sup> for CFC-11, 6% or 0.005 pmol kg<sup>-1</sup> for CFC-12 and 4% or 0.04 fmol kg<sup>-1</sup> for SF<sub>6</sub>.

A number of water samples had anomalously high CFC/SF<sub>6</sub> concentrations relative to adjacent samples. These samples occurred sporadically during the cruise and were not clearly associated with other features in the water column (e.g., anomalous dissolved oxygen, salinity, or temperature features). This suggests that these samples were probably contaminated with CFCs/SF<sub>6</sub> during the sampling or analysis processes.

Measured concentrations for these anomalous samples are included in the data file, but are given a quality flag value of either 3 (questionable measurement) or 4 (bad measurement). For CFC-11, ~2% of the water sample concentrations reported were assigned a flag of 3 and ~2% assigned a flag of 4. For CFC-12 ~68% of samples were assigned a flag of 3 (primarily because of the correction factor applied after Station 13) and ~ 2% assigned a flag of 4. For SF<sub>6</sub>, ~3% of water samples were assigned a flag of 3 and ~ 2% assigned a flag of 4. A quality flag of 5 was assigned to samples which were drawn from the rosette but never analyzed due to a variety of reasons (e.g., leaking stopcock, plunger jammed in syringe barrel, etc).

## References

Bullister, J.L. and R.F. Weiss (1988): Determination of CC<sub>13</sub>F and CC<sub>12</sub>F<sub>2</sub> in seawater and air, Deep-Sea Research, 25, 839-853.

Bullister, J.L., and T. Tanhua (2010): Sampling and measurement of chlorofluorocarbons and sulfur hexafluoride in seawater. In The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. E.M. Hood, C.L. Sabine, and B.M. Sloyan (eds.), IOCCP Report Number 14, ICPO Publication Series Number 134. Available online at <http://www.go-ship.org/HydroMa>

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